

Stress effect on cycle properties of the silicon thin-film anode

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Abstract

Si thin-film electrodes were deposited by rf magnetron sputtering method, and stress variation during charge and discharge process was measured. When Si reacts with Li forming several alloy phases sequentially, large volume expansion occurs inducing compressive stress. On Li insertion to 0 V, the formation of $\text{Li}_{4.4}\text{Si}$ phase, which have a volume three or four times larger than Si, causes a microcracking in the electrode, thereby the cycle performance is deteriorated. However, by limiting the lower cut-off voltage to 0.1 V, the cyclability was improved significantly. This is attributed to the reduction of the crack formation due to volume expansion, as inferred from the stress variation profile. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Si is one of the promising anode material for microbatteries, because of its large reversible accommodation capacity of Li and little irreversible reaction which happens in the first cycle. About 1 mol of Si can react with about 4.4 mol of Li to form several intermediate Li–Si alloys up to $\text{Li}_{4.4}\text{Si}$ at 400°C [1,2]. It corresponds to a capacity of 4000 mAh/g. Electrochemical Li–Si reaction occurs between 0 and 0.3 V against Li/Li^+ , so that high-energy density battery can be realized.

However, it was reported that Si powders experience large volume change during continuous Li insertion and extraction process, which leads to a pulverization of Si powders, and it eventually results in a fast capacity fading [3,4]. Especially, large volume change of thin-film anode can cause a serious problem, poor adhesion at the interface between the anode and solid electrolyte thin-film, which leads to the increase of cell impedance and the poor cycle performances.

In this paper, we investigated the stress change during electrochemical Li insertion into and extraction from the Si thin-film electrode and its relation to cycle performances.

2. Experimental

Si thin-film electrodes were deposited by rf magnetron sputtering Si target (2 in. in diameter) onto a Cu foil substrate (12 mm in diameter) for cycling test and on the glass/Ti/Cu substrate (130–160 μm in thickness, 2 mm in width, 35 mm in length) for the stress measurement in the Ar ambient. The Ti glue layer was pre-deposited to improve the adhesion between Cu current collecting layer and glass substrate. The base and working pressure were 2×10^{-6} Torr and 5 mTorr, respectively. Si thin-films with 350 Å in thickness were obtained at 150 W in rf power for 1 min. The substrate holder was water-cooled during deposition.

A 2016 coin type cell and a three-electrode beaker type cell were employed to test cycle properties and to examine the stress variation during Li insertion and extraction process. The Si thin-film electrode served as the working electrode, and high-purity metallic Li sheet was used as a reference and counter electrode. The electrolyte consisted of 1 M LiPF_6 in a nonaqueous solution of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. Charge–discharge measurements were performed with constant current.

An optical cantilever method was used to measure the stress induced by the volume change of Si thin-film electrode during the electrochemical Li insertion and extraction

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process. He–Ne laser with the wavelength of 633 nm was used as the incident beam. The positional change of the laser beam reflected from the backside of the electrode was detected on the one-dimensional linear type photo diode. The signal from the photodiode was converted to the voltage signal.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the Si thin-film electrode deposited on Cu substrate. We could not observe any reflections except those of copper substrate. So, we defined the structure of the Si thin-film as X-ray amorphous. X-ray amorphous structure is usually more open compared with well crystallized one. This relatively open structure would make the lattice expansion moderately [5].

Fig. 2 shows the stress variation, as represented by voltage profile, in the Si thin-film electrode on the glass substrate, when Li/thin-film Si cell is discharged and charged with constant current rate of $125 \mu\text{A}/\text{cm}^2$. The right side voltage is associated with the deflection angle, in which the negative sign means that the compressive stress is induced. A differential capacity plot calculated from the voltage profile is

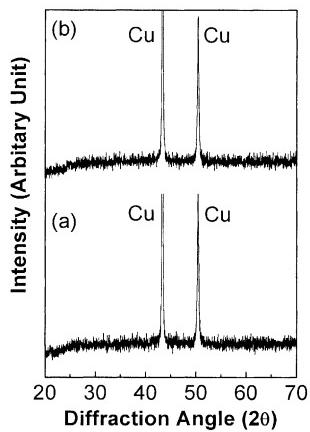


Fig. 1. XRD patterns of Si thin-film: (a) Cu substrate; (b) deposited 350 Å in thickness.

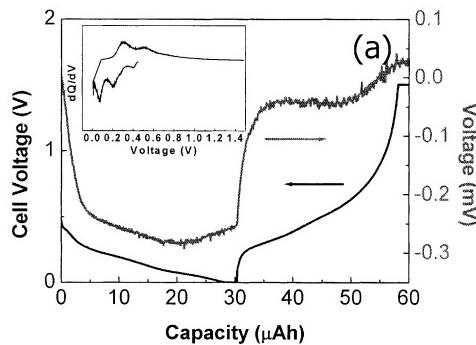
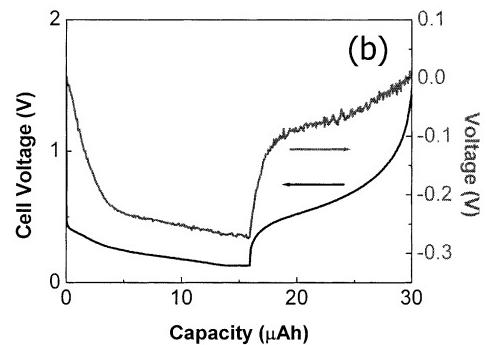


Fig. 2. Voltage profiles and stress variation. The plot in a inner box shows the differential capacity vs. cell voltage (dQ/dV): (a) 0–1.5 V; (b) 0.1–1.5 V.

shown in the inner box. When the cell is discharged to 0 V, two peaks are observed at about 0.08 and 0.24 V, indicating that the discharge process occurs basically in two steps. The derivative curve is also similar to that for the powdered Si sample [3]. The similarity suggests a common mechanism for the insertion of Li ions in both of powdered and thin-film Si electrodes. It has been reported that the Si reacts with Li to form Li_2Si at 0.25 V and $\text{Li}_{4.4}\text{Si}$ at 0.1 V [3].

During the Li insertion process, the stress variation occurs through sequential three steps. In the initial stage of Li insertion to the cell voltage of 0.3 V, the compressive stress increases steeply. It is because Si is supersaturated with Li at the surface region, and Li_2Si phase is first formed, while the near substrate region is still in the unreacted Si. The formation of Li_2Si phase, having a volume two times larger than Si, near the surface of the thin-film Si electrode leads to large volume expansion. The second step occurs in a cell voltage region from 0.3 to 0.1 V, in which Li_2Si phase is formed over the electrode film. In this stage, the compressive stress in the electrode film continuously increases with reduced slope. On the other hand, noticeably, the compressive stress decreases on further Li insertion to the cell voltage of 0 V, which corresponds to the third stage. $\text{Li}_{4.4}\text{Si}$ phase formed during the third stage have the volume of four times larger than Si, and the formation of this phase leads to a very large volume expansion of the electrode. At this point, the large volume expansion causes the electrode to crack, thereby relieving the stress. The cracks on the Si surface were observed by SEM (not shown here). Upon charge, Li is firstly extracted from the surface of the electrode film, which rapidly relieve the compressive stress as a converse phenomenon of that observed in the initial stage of Li insertion. In case of limiting lower cut-off voltage to 0.1 V, the third stage related to the stress variation during insertion has not been observed and the stress variation during cycling was also reversible. This seems to indicate that the charge and discharge reaction proceeds without electrode cracking.

Fig. 3 shows the cycle performances of the Si thin-film electrode for the lower cut-off voltage of 0 and 0.1 V. By limiting the lower cut-off to 0.1 V, the cyclability is improved, significantly. From the viewpoint of stress and volume change, we believe that this improvement of



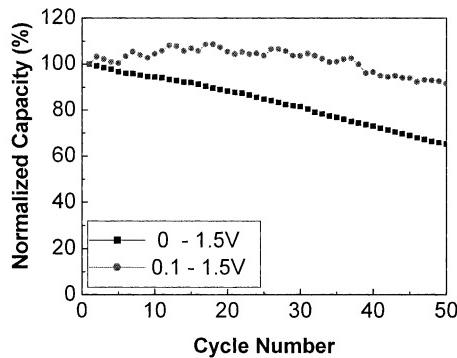


Fig. 3. Cyclability of the Si thin-film electrode.

cyclability is associated with the reduction of the crack formation due to volume expansion by limiting the formation of large volume phase, $\text{Li}_{4.4}\text{Si}$.

4. Conclusion

The stress variation during charge and discharge process in the Si thin-film electrode was measured. The volume

expansion by Li insertion induced a compressive stress in the electrode. In the case of Li insertion to 0 V, the stress variation occurred sequentially in three steps. It appeared that microcracking in the electrode occurred in the range of 0–0.1 V corresponding to the third step of stress variation. Limiting the lower cut-off voltage to 0.1 V versus Li/Li^+ significantly improved the cycle performance. This was attributed to the prevention of microcracking, as inferred from the stress variation profile.

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